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(54) Title: PROCESS FOR THE PRODUCTION OF HIGH PURITY ZIRCONIA

(57) Abstract

A process for the production of high-purity zirconia, which comprises the steps of leaching dissociated zircon or other zirconiferous material with concentrated sulphuric acid, and thereafter separating the resulting zirconium-containing product from the unattacked silica, characterized in that water formed during the leaching reaction is continuously removed from the system preferably by using an air-cooled reflux condenser to maintain the temperature in the range from about 300°C to the maximum boiling point.

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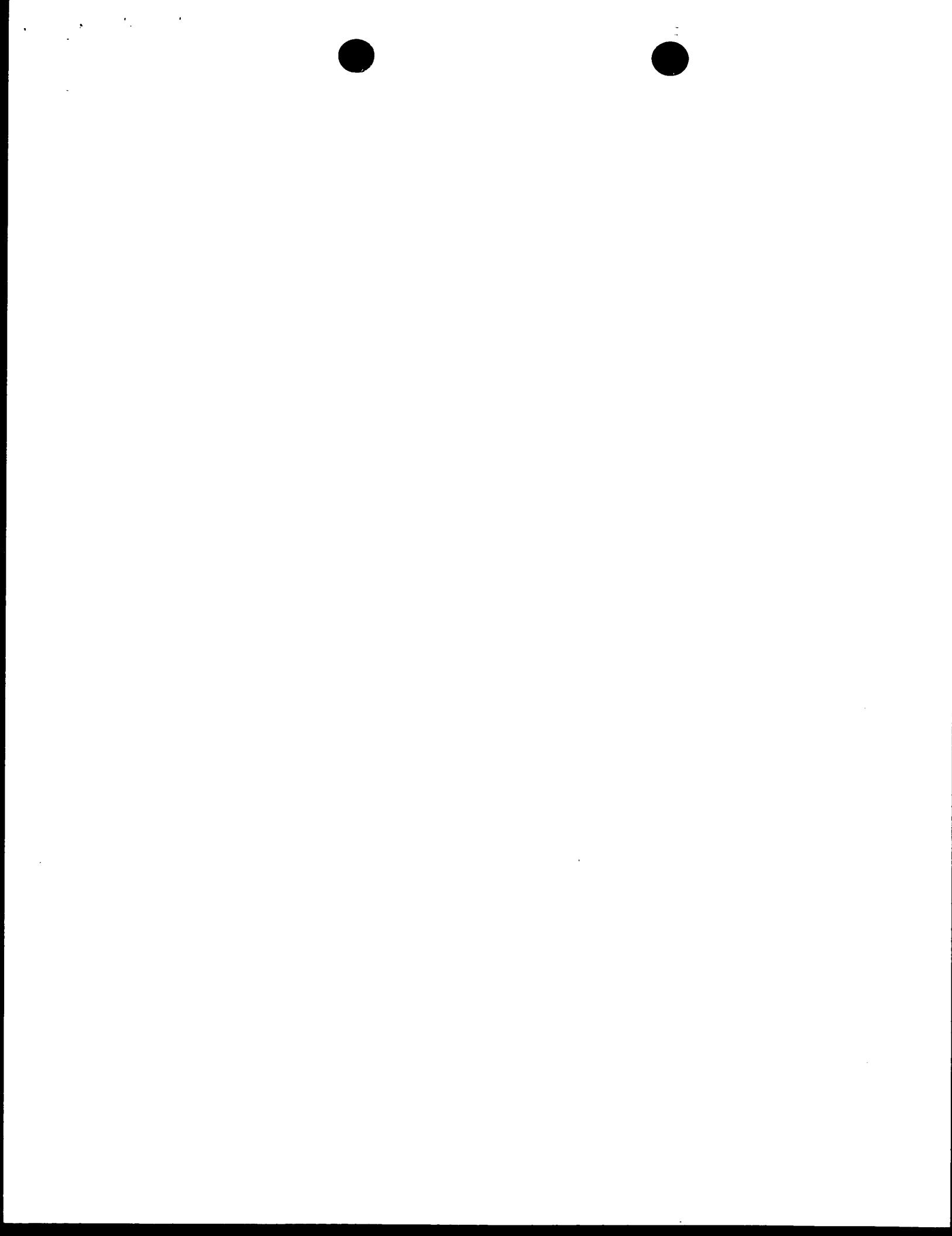
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thereof) followed by chemical treatment of the decomposition products to produce pure zirconia.

Chemical decomposition of zircon can be
5 accomplished by sintering with alkali or alkaline earth oxides. Sodium hydroxide or sodium carbonate are usually used for this purpose and the reaction can be controlled to produce a product consisting of sodium zirconate and sodium silicate. This product is
10 then leached with water to dissolve the sodium silicate and hydrolyse the sodium zirconate to crude hydrous zirconia, which is then further purified. For example, the crude zirconia may be dissolved in hydrochloric acid followed by sulphuric acid and
15 reprecipitated as zirconium sulphate (e.g., $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) by adjustment of the sulphate/water ratio of the solution or as hydrated zirconium oxide by precipitation with ammonia.

20 Zircon can also be completely dissociated by heating at temperatures in excess of 1800°C, for example using a plasma arc furnace. When zircon sand is injected into the plasma arc, it melts and dissociates into zirconia and silica. On rapid
25 cooling, solidification occurs with the formation of extremely small zirconia crystallites in an amorphous silica matrix.

Dissociation of zircon can also be accomplished
30 by heating in a conventional electric furnace (operating at about 2000°C) or in a so-called "advanced electric reactor" (AER) furnace operating at about 2400°C. Furnaces of this latter type are



described in International Patent Publication
No. WO 85/04158 and the references cited therein.

5 The dissociated zircon product, however produced,
may then be chemically treated to separate the
zirconia from the silica. There are two basic
approaches:

10 (a) Leaching with caustic soda to dissolve the silica
and leave the zirconia crystallites as a
relatively pure product.

15 (b) Treating with sulphuric acid to convert the
zirconia to zirconium sulphate which can be
separated from the unattacked silica.

20 The thermal-dissociation/alkali-leach process
suffers from two main disadvantages. Firstly, the
product seldom contains more than 99.4% ZrO_2 and must
be further purified for uses requiring very high
purity. Additionally, while the by-product of
alkaline leaching, sodium metasilicate has a ready
market in some countries for the detergent industry,
there is little demand for it in Australia and
25 disposal thus presents further problems.

30 Japanese Patent Publication No. 23975/1969
describes a process for producing high purity zirconia
which involves

- dissociation of zircon by heating in an electric
furnace (1900-2000°C) followed by rapid quenching

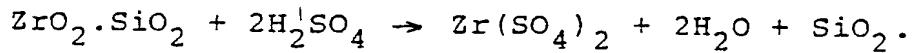
- crushing the dissociated material to 100-300 mesh particles
- treating the particles with concentrated sulphuric acid at 5 $200^\circ - 300^\circ$ for 4-5 hours then $300^\circ - 400^\circ$ for 3-4 hours
- 10 - leaching the thus-treated material with water to extract the zirconia as zirconium sulphate and subsequent chemical treatment to produce hydrated zirconium oxysulphate which is then pyrolyzed to give zirconia.

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The overall yield of the process is 80-90% based on the zirconia content of the starting ore.

20 The need for grinding of the dissociated ore and the long acid-treatment times constitute serious economic disadvantages for this process.

25 We have now found that the efficiency of sulphuric acid leaching of dissociated zircon can be greatly enhanced if proper attention is paid to the removal from the system of the water which is produced during leaching, according to the reaction



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Providing this water is continuously removed from the reaction system, thus maintaining constant acid concentration and temperature, leaching kinetics are

considerably improved and satisfactory leaching can be achieved in 2 to 3 hours.

5 This procedure can also be applied, with advantage, to the leaching of other zirconiferous materials, such as baddeleyite, or impure zirconia from natural or artificial sources, such as partially-leached zirconia, for example as produced by alkali leaching of thermally-dissociated zircon.

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There is a considerable body of prior art (for example US Patent No. 2,387,046), relating to the use of sulphuric acid to refine impure zircon and treat low silicon zirconia-based ores.

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15 The prior art indicates that considerable difficulty may be encountered when the silica content of zirconia-containing ores is greater than 10%, particularly when it is present as $ZrSiO_4$ rather than 20 free silica (see U.S. Patent No. 2,387,046). Consequently, processes have been developed which involve preliminary steps for breaking the ZrO_2/SiO_2 bond and reducing the SiO_2 level, e.g. by fusion with caustic soda (U.S. 2,387,046, U.S. 3,398,005).

25

Such caustic-treated materials may also be treated by the method of the present invention.

30 Accordingly, the present invention provides a process for the production of high-purity zirconia, which comprises the steps of leaching dissociated zircon or other zirconiferous

material with concentrated sulphuric acid, and thereafter separating the resulting zirconium-containing product from silica or any other unattacked impurity, characterized in that water formed during 5 the leaching reaction is continuously removed from the system.

Preferably, the water removal is effected in such a way as to maintain the sulphuric acid concentration 10 at a substantially constant concentration of about 98%, so that the leaching temperature can be maintained in a range from about 300°C to the maximum boiling point of the concentrated acid, preferably in the range 320°C ± 5°C.

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Zirconia can then be recovered from the zirconium sulphate produced during leaching by methods known per se, or by those described hereinafter.

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As previously indicated, the prior art shows that it is preferable to finely grind dissociated zircon before leaching.

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In the present process, however, at least for some dissociated products, grinding may be unnecessary. For example, zircon dissociated using the AER furnace can usually be satisfactorily leached without grinding.

30

Separation of the excess acid, anhydrous zirconium sulphate and silica may be carried out by filtration or any other suitable known method. The excess acid may be filtered from the solid anhydrous zirconium sulphate and silica (and any unreacted

dissociated zircon). The solid mixture of silica and anhydrous zirconium sulphate may be leached with water to dissolve the zirconium sulphate which is then separated from the silica, by filtration.

5

The resulting solution is treated to precipitate hydrated zirconium sulphate, e.g., by evaporation and/or other adjustment of the sulphate/water ratio.

10

Alternatively, a measured amount of water can be added to the reaction products prior to the removal of the excess acid. Addition of water to the acid slurry generates heat and dissolves the anhydrous zirconium sulphate. The hot zirconium sulphate solution may be

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filtered from the silica (and any unreacted dissociated zircon). On cooling, the filtrate deposits hydrated zirconium sulphate.

20

In either case, the hydrated zirconium sulphate product is usually mainly in the form of the tetrahydrate. This product can be pyrolyzed to produce high purity zirconia and sulphur trioxide, which can be recycled, to the leaching stage, if desired.

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An alternative method of producing zirconia from zirconium sulphate solution is to adjust the solution pH, e.g., by using ammonia, urea or sodium hydroxide, to precipitate hydrated zirconium oxide which on 30 calcination gives zirconia.

The invention is illustrated by the following examples.

EXAMPLE 1

(a) 100g samples of dissociated zircon of various particle sizes and produced by varying techniques were 5 digested with 330g of 98% sulphuric acid in a 500 cm³ glass reactor fitted with a glass stirrer rotating continuously at 600 rev/min, a thermo-pocket containing a thermometer (or pyrometer) and an air-cooled reflux condenser. The reactor was heated 10 by a heating mantle. The air-cooled condenser returned the refluxing sulphuric acid to the reactor whilst allowing the water produced from the reaction to escape. In this way, the refluxing sulphuric acid solution was maintained at a concentration of 98% and 15 the reaction temperature was maintained at approximately 320°C during the course of the reaction.

Heating and stirring were continued for 4 hours.

20 The progress of the reaction was monitored by removing samples of the refluxing suspension at known time intervals. These samples were immediately quenched, then washed free of soluble zirconium sulphate and the solid residue analysed for SiO₂ and 25 residual ZrO₂ by XRF. The percentage of ZrO₂ leached from each sample of dissociated zircon was calculated.

(b) As a comparison, the leaching experiments described above were repeated except that the 30 air-cooled reflux condenser was replaced by a water-cooled reflux condenser which refluxed both the acid and the water produced during the reaction to the

reactor. The water content of the refluxing sulphuric acid solution increased as the reaction proceeded, thereby causing the reaction temperature to fall. Heating and stirring were continued for 4 hours and the progress of the leaching reaction was monitored, as in the earlier tests.

The results for the two series of leaching tests are given in Table 1. They clearly show that improved leaching rates are obtained when the leaching is carried out at constant temperature, in accordance with the present invention.

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Table 1. Leaching rates of dissociated zirconia.

Dissociated zircon used for reaction	Percentage ZrO_2 leached					
	Total reflux leach time (h)			Constant temperature leach time (h)		
	1	2	4	1	2	4
Unground AERDZ* sand	51.7	66.8	81.3	52.3	77.2	92.8
Ground AERDZ sand, -45 μm	80.3	88.5	93.7	92.7	95.1	95.1
Unground AERDZ flour	62.2	69.0	86.1	68.3	81.7	86.0
Unground PDZ *	26.0	44.9	55.5	26.0	46.6	56.8
Ground PDZ, -150+106 μm	35.3	51.9	66.5	36.9	58.9	73.3
Ground PDZ, -75+45 μm	54.4	69.9	82.3	62.2	83.9	89.8

*AERDZ = Advanced Electric Reactor Dissociated Zircon.
PDZ = Plasma Dissociated Zircon.

EXAMPLE 2

A leaching test using PDZ (-75+45 μm) was performed as described in Example 1. After 4 hours at 5 constant temperature, heating was terminated and the suspension filtered. The solid residue was treated with distilled water to dissolve the zirconium sulphate. The water-insoluble silica and unreacted dissociated zircon were filtered from the zirconium sulphate solution which was then evaporated at its 10 boiling point under atmospheric pressure until crystallization commenced. Crystallization was completed by allowing the solution to cool. The $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ crystals were filtered, washed with acetone, dried at 100°C, then calcined at 950°C to 15 produce high-purity zirconia (ZrO_2).

A typical product contained the following levels of impurities (ppm): SiO_2 , 100; Al_2O_3 , 220; Fe_2O_3 , 20 130; and TiO_2 , 90.

EXAMPLE 3

A leaching test using 100g of PDZ (-75 + 45 μm) was 25 performed as described in Example 1. After 4 hours at constant temperature, heating was terminated and the suspension filtered. The solid residue was treated with 260g of water to dissolve the zirconium sulphate. The water-insoluble silica and unreacted dissociated 30 zircon were filtered from the zirconium sulphate solution. 370g of 98% H_2SO_4 was added to the filtrate to effect quantitative crystallization of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$.

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EXAMPLE 4

A leaching test using 100g of PDZ (-75 + 45 μ m) was performed as described in Example 1. After 4 hours at 5 constant temperature, heating was terminated and the suspension allowed to cool. 150g of water was then added to the stirred suspension to dissolve the zirconium sulphate. The resulting hot suspension was filtered to remove the water insoluble silica and 10 unreacted dissociated zircon. On cooling, the filtrate deposited $Zr(SO_4)_2 \cdot 4H_2O$ crystals quantitatively.

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CLAIMS

1. A process for the production of high-purity zirconia, which comprises the steps of leaching dissociated zircon or other zirconiferous material with concentrated sulphuric acid, and thereafter separating the resulting zirconium-containing product from silica or any other unattacked impurity, characterized in that water formed during the leaching reaction is continuously removed from the system.
2. A process as claimed in Claim 1, characterized in that water removal is effected in such a way as to maintain the sulphuric acid concentration at about 98%, so that the leaching temperature is in the range from about 300°C to the maximum boiling point of the concentrated acid.
3. A process as claimed in Claim 2, characterized in that the leaching temperature is in the range 320°C ± 5°C .
4. A process as claimed in any one of Claims 1 to 3, characterized in that the dissociated zircon or other zirconiferous material is finely ground prior to leaching.
5. A process as claimed in Claims 1 to 4, characterized in that dissociated zircon is used which has been produced by thermal dissociation in an advanced electric reactor furnace.

6. A process as claimed in Claims 1 to 5, characterized in that dissociated zircon is used which has been produced in a plasma arc furnace.
7. A process as claimed in any of Claims 1 to 6, characterized in that following leaching excess acid is separated from the zirconium-containing product and the product is leached with water to produce a zirconium sulphate solution which is separated from the silica and other insoluble impurities.
8. A process as claimed in any one of Claims 1 to 6, characterized in that following leaching, water is added to reaction products in an amount sufficient to form a hot solution of zirconium sulphate which is separated from the silica and other insoluble impurities while still hot.
9. A process as claimed in Claim 7 or Claim 8, characterized in that the zirconium sulphate solution is treated to precipitate hydrated zirconium sulphate.
10. A process as claimed in Claim 7, characterized in that after removal of the silica and other insoluble impurities, hydrated zirconia sulphate is precipitated from the solution by adjustment of the sulphate/water ratio.
11. A process as claimed in Claim 7, characterized in that after removal of the silica and other insoluble impurities, hydrated zirconia sulphate is precipitated from the solution by evaporation of the solution.

12. A process as claimed in Claim 8, characterized in that after removal of the silica and other insoluble impurities, the solution is cooled to precipitate hydrated zirconium sulphate.

13. A process as claimed in any one of Claims 9 to 12, characterized in that the zirconium sulphate is pyrolyzed to produce high purity zirconia.

14. A process as claimed in any one of Claims 7 to 12, characterized in that the solution of zirconium sulphate or a solution of the redissolved hydrated zirconium sulphate is subjected to pH adjustment to precipitate hydrated zirconium oxide.

15. A process as claimed in Claim 14, characterized in that the pH of the solution is adjusted by addition of ammonia, urea or sodium hydroxide.

16. A process as claimed in Claim 14 or Claim 15, characterized in that the hydrated zirconium oxide is calcined to produce zirconia.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/AU 86/00018

III. CLASSIFICATION OF SUBJECT MATTER (If more than one class, list them in order of priority)

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl. 4 C22B 34/14, C01G 25/02, 25/06

II. FIELDS SEARCHED

Minimum Documentation Searched *

Classification System	Classification Symbols
IPC	C22B 34/14, C01G 25/02, 25/06
US Cl.	423/82

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched *

AU ; IPC as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT*

Category *	Citation of Document, 11 with indication, where appropriate, of the relevant passages 12	Relevant to Claim No. 13
X	AU,B, 36935/58 (224798) (BRITISH TITAN PRODUCTS LTD) 9 October 1958 (09.10.58) See pages 5,6 & 8, Example 1	(1)
X	US,A, 1502422 (COOPER) 22 July 1924 (22.07.24) See page 1, col. 2, lines 80-82; page 2 col. 1, lines 45-50; claims 4-5	(1 & 4)
X	US,A, 1618286 (KINZIE) 22 February 1927 (22.02.27) See page 2, col. 1, lines 41-54	(1,2,4,5)
A	JP,A, 44-23975 (YOKOZAWA CHEMICAL INDUSTRY CO. LTD) 11 October 1969 (11.10.69) (Chem. Abstract 72-33812f)	

* Special categories of cited documents 10

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search
1 April 1986 (01.04.86)

Date of Mailing of this International Search Report

(23-04-86) 23 APRIL 1986

International Searching Authority

Australian Patent Office

Signature of Authorized Officer

